

ARMY RESEARCH LABORATORY



Analysis of Ferroelectric Thin Films Grown by MOD Process

by Robert Hoffman and Wesley Tipton

ARL-MR-375

February 1998

DTIC QUALITY INSPECTED

19980317 162

Approved for public release; distribution unlimited.

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

Army Research Laboratory

Adelphi, MD 20783-1197

ARL-MR-375

February 1998

Analysis of Ferroelectric Thin Films Grown by MOD Process

Robert Hoffman and Wesley Tipton

Sensors and Electron Devices Directorate

sponsored by

Defense Advanced Research Projects Agency

3701 N. Fairfax Drive

Arlington, VA 22203

Abstract

The Army Research Laboratory (ARL) has performed ferroelectric characterization testing of thin film ferroelectric samples provided by Raytheon TI Systems (RTIS) for the DARPA (Defense Advanced Research Projects Agency) uncooled detector materials program. The samples measured at ARL, produced by the metal-organic decomposition (MOD) method, have hysteresis loop characteristics, remanant polarization, and dielectric constant and resistivity values commensurate with measurements made at RTIS. RTIS projections show that Ca- and Sn-doped samples should achieve a projected noise equivalent temperature difference (NETD) of 13.8 mK with 48.5- μ m pixels and 26.5 mK with 50- μ m pixels, respectively.

Contents

1. Introduction	1
2. Sample Fabrication	1
3. Hysteresis Loop and Loss Tangent Measurements	3
4. Test Results	4
5. Conclusions	9
Distribution	11
Report Documentation Page	13

Figures

1. Room temperature PLZT phase diagram	1
2. Film structure of MOD deposited capacitors	2
3. Hysteresis loop of RTIS sample PBT-20 with imprinting	5
4. Hysteresis loop of RTIS sample FET 170 showing effect of thermal damage	5
5. "Ideal" hysteresis loop of ARL sample	6
6. Hysteresis loop of typical RTIS sample	6
7. RTIS sample PBT-10 showing asymmetric hysteresis loop	8
8. Hysteresis loop of RTIS sample PCT-30 showing effect of multiple cycles	9

Tables

1. Summary of hysteresis loop measurements	3
2. Summary of film structure and treatment	4
3. Electrical properties of substituted lead titanates	8

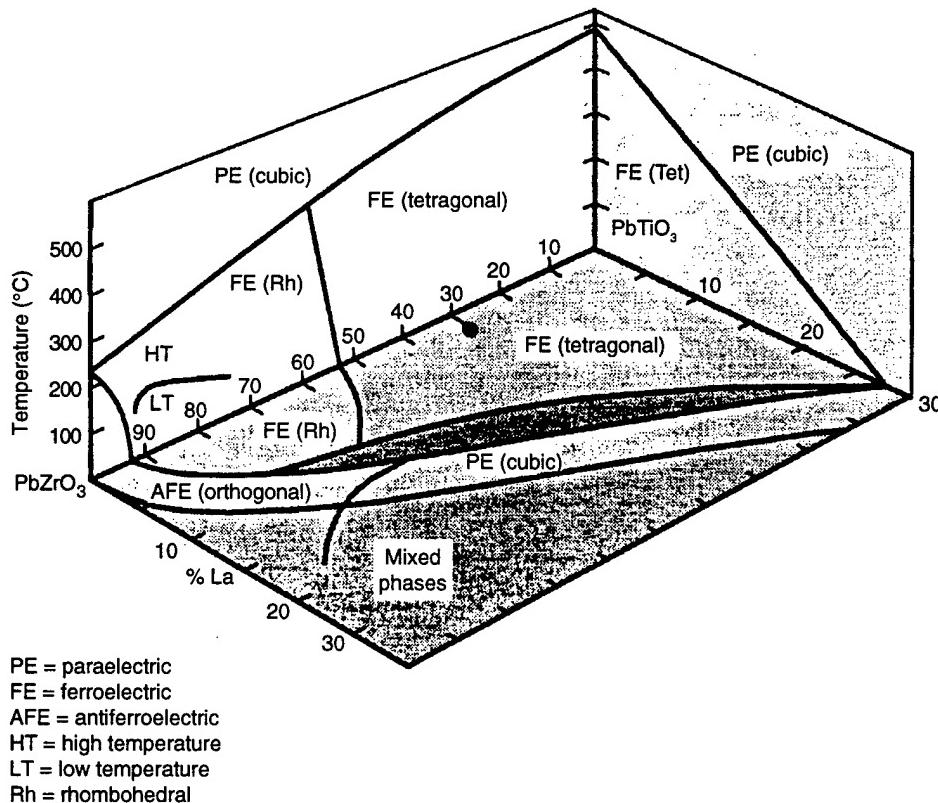
1. Introduction

The Army Research Laboratory (ARL) has performed ferroelectric characterization testing of thin film ferroelectric samples provided by Raytheon TI Systems (RTIS). ARL has endeavored to create state-of-the-art ferroelectric testing facilities in-house in order to provide an independent system of verification of the ferroelectric thin film materials produced under a contract with RTIS. Specifically described here are hysteresis loop measurements made at ARL. Remanent polarization, dielectric constant, and resistivity data are derived from the hysteresis loop data.

2. Sample Fabrication

The samples sent by RTIS were a part of a study to determine the effects of lead nonstoichiometry and electrode configuration on the ferroelectric characteristics of the films. The composition of the lead lanthanum zirconium titanate (PLZT) films in all cases was (3/30/70), meaning the mole fraction was 0.03 for lanthanum, 0.3 for zirconium, and 0.7 for titanium. The lead concentration was enhanced in each case by 10 mol % to compensate for lead loss during annealing. Figure 1 shows a phase diagram showing the various ferroelectric, antiferroelectric, and paraelectric phases with respect to composition. The dot at 3 mol % La, 30 mol % Zr, and 70 mol % Ti is within the tetragonal ferroelectric phase region of the phase diagram.

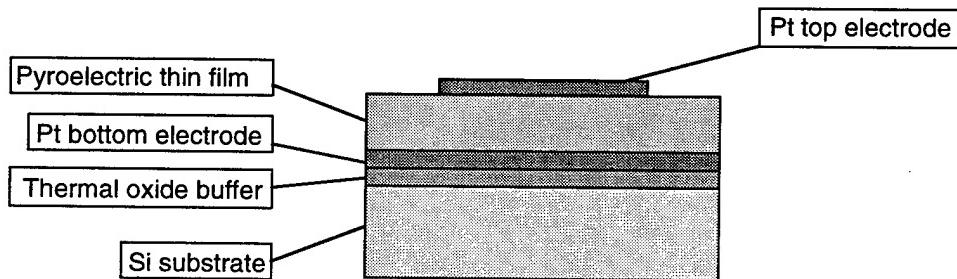
Figure 1. Room temperature PLZT phase diagram.



The samples were made by the metal-organic decomposition (MOD) method, which has proven to be a very economical and efficient method of producing high-quality thin films of ferroelectric materials. MOD involves the deposition on a rotating substrate of a solution of the various component ions of the material. Typically, acetates or acetate derivatives of the metal ions are dissolved in an aqueous or alcohol solution in the correct stoichiometric proportions. The solution is dispensed onto a substrate rotating at several thousand revolutions per minute. Upon contact, the solution evaporates, leaving an amorphous film of the acetates. Pyrolyzing at several hundred degrees Celsius removes most of the organic residue. Calcining at higher temperatures oxidizes away the residual carbon and crystallizes the ferroelectric in the perovskite phase.

All the samples produced under this contract were annealed in a rapid thermal annealer (RTA). The principal differences in these particular samples are in the ferroelectric film thickness, the lead stoichiometry, and the top/bottom electrode thickness (and manner of deposition). The samples were provided with a bottom contact and with square top contact pads of varying sizes, from 0.25 mm on a side to 1.0 mm on a side (fig. 2).

Figure 2. Film structure of MOD deposited capacitors.



3. Hysteresis Loop and Loss Tangent Measurements

We performed the hysteresis loop measurements with a Radian Technologies RT-66A ferroelectric measurement system. We used a Wentworth probe station equipped with a stereo microscope to make electrical contact to the sample. The data were acquired with the software supplied with the RT-66A on a standard 386 PC. The RT-66A system is capable of applying up to 40 V peak-to-peak voltage to the sample. The RT-66A provides complete sample information such as P_s (saturation polarization, $\mu\text{C}/\text{cm}^2$), P_r (remanent polarization, $\mu\text{C}/\text{cm}^2$), V_c (coercive field, V), ϵ_r (relative dielectric constant), and R_y (resistivity, $\Omega \text{ cm}$). The loss tangent data were obtained as a function of frequency from 100 Hz to 1 MHz by a Hewlett-Packard HP4194A impedance analyzer. RTIS did not specify at what frequency their $\tan \delta$ measurements were taken; however, at 100 Hz, $\tan \delta$ is at a minimum in all cases observed, so all ARL measurements were made at 100 Hz. Although the measurements are not a complete or definitive diagnostic of ferroelectric thin film performance, they provide a needed guidepost to gauge progress in thin film ferroelectric development. Table 1 summarizes both the RTIS data and the ARL data. Table 2 summarizes the film structure and annealing treatments (where available) of each film.

Table 1. Summary of hysteresis loop measurements.

Data	Sample ID	ϵ_r	$\tan \delta$	P_s ($\mu\text{C}/\text{cm}^2$)	P_r ($\mu\text{C}/\text{cm}^2$)	V_c (V)	R_y ($\Omega \text{ cm}$)
RTIS	161	490	0.04	34	11	2.3–3	10^{10} – 10^{11}
ARL	161	341	0.05	34.6	8.6	3.3	1.7×10^{10}
RTIS	163	530	0.013	25–34	11–15	4.7	10^{10} – 10^{11}
ARL	163	202	0.016	31.0	11.0	4.3	5.1×10^{11}
RTIS	170	320	0.013	26	11	4.5	10^{10}
ARL	170	200	0.026	17.1	1.99	0.4	3.1×10^{11}
ARL	170	268	—	6.1	5.1	–8.0	1.1×10^{12}
RTIS	164	410	0.030	19–28	6–10	3.7	10^6 – 10^{11}
ARL	164	403	0.010	26.1	14.1	1.4	1.6×10^3
ARL	030	1013	0.026	27.4	7.8	5.7	1.5×10^{11}
RTIS	results not available						
ARL	280	859	0.028	24.2	5.1	2.5	1.3×10^8
RTIS	results not available						
ARL	137	404	0.029	33.1	9.6	4.3	4.1×10^{10}
RTIS	results not available						

Table 2. Summary of film structure and treatment.

Sample ID	Film thickness (Å)	Ti/Pt bottom electrode	Top electrode	Anneal schedule
161	1500	CRL	Pt (Hum)	600/10 s
163	1500	CRL	Ti/Pt (Hum)	600/10 s
164	1500	CRL	Ti/Pt (Tem)	600/10 s
170	3000	Tem	Pt (Hum)	600/30 s

Tem = Temescal deposition unit

CRL = RTIS Corporate Research Laboratory deposition facility

Hum = Hummer sputter deposition unit

4. Test Results

The ARL data represent data taken on a single pad, or in the case of sample 170, two pads on the same sample. The ARL data closely track the RTIS data except for the relative dielectric constant ϵ_r , for which we consistently found lower measurements. We believe that sample 170 was thermally compromised before it was sent to ARL, which would explain the dielectric anomalies observed and its crazed appearance.

Several anomalies appear in the hysteresis loop data as well. For example, in sample 163 the hysteresis loop is discontinuous, as it is with samples 170, 164, 280, and 137. In samples 163, 164, 280, 137, and PBT-20 (fig. 3), it appears that there are two values for the remanant polarization on the negative part of the loop. This phenomenon, known as imprinting, results when the film has a preferred polarization at zero applied field. Most likely, imprinting is due to ferroelectric domains that are "pinned" in the film because of strain induced during deposition and annealing. One pad of sample 170 exhibits even more unusual behavior. The loop is decidedly asymmetric, yielding a V_c that is negative (fig. 4), possibly due to thermal damage. The other pad of sample 170 investigated yields a curve that is generally symmetric, but the shape resembles that of an antiferroelectric material, with two almost separate loops seen in the positive and negative quadrants. The behavior of sample 161 appears normal in most respects, except that almost 40 V of peak-to-peak voltage is required to obtain the hysteresis loop. This voltage seems excessive compared to those required for other films grown at other facilities. For example, sample PZT 102491B-1, a thin film of lead zirconium titanate (PZT) shown in figure 5, exhibits the expected behavior of a thin film ferroelectric material. This film exhibits symmetric behavior and saturates at only 20 V peak-to-peak. A "typical" RTIS hysteresis loop is shown in figure 6. As reported by RTIS, the only difference in the supplied samples lies in the electrode systems and the heating schedule used to anneal the film. It would appear that the heating schedule used to anneal sample 170 has thermally damaged the film. In addition, the relatively flat tan δ versus frequency performance of this film from 100 Hz to 1 MHz suggests that it is behaving more like a lossy dielectric than a ferroelectric material.

Figure 3. Hysteresis loop of RTIS sample PBT-20 with imprinting.

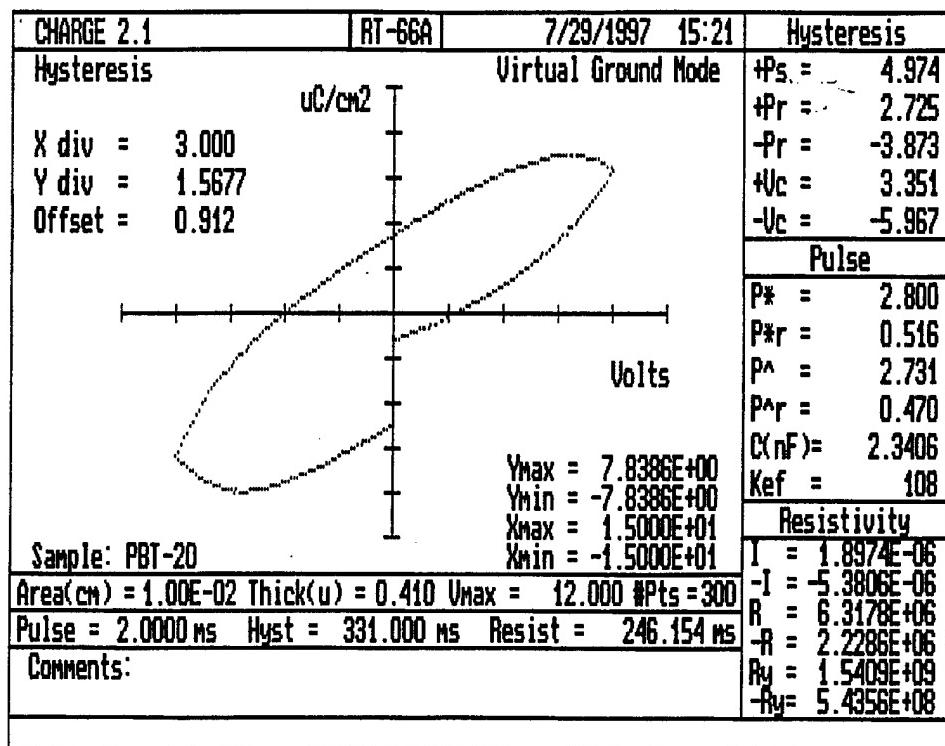


Figure 4. Hysteresis loop of RTIS sample FET 170 showing effect of thermal damage.

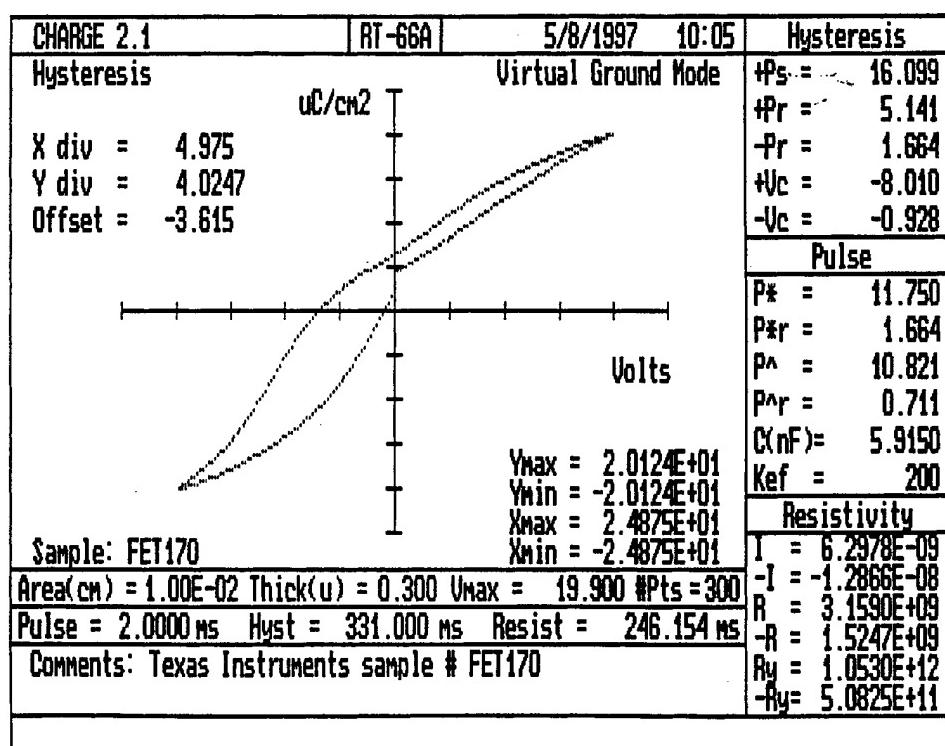


Figure 5. "Ideal" hysteresis loop of ARL sample.

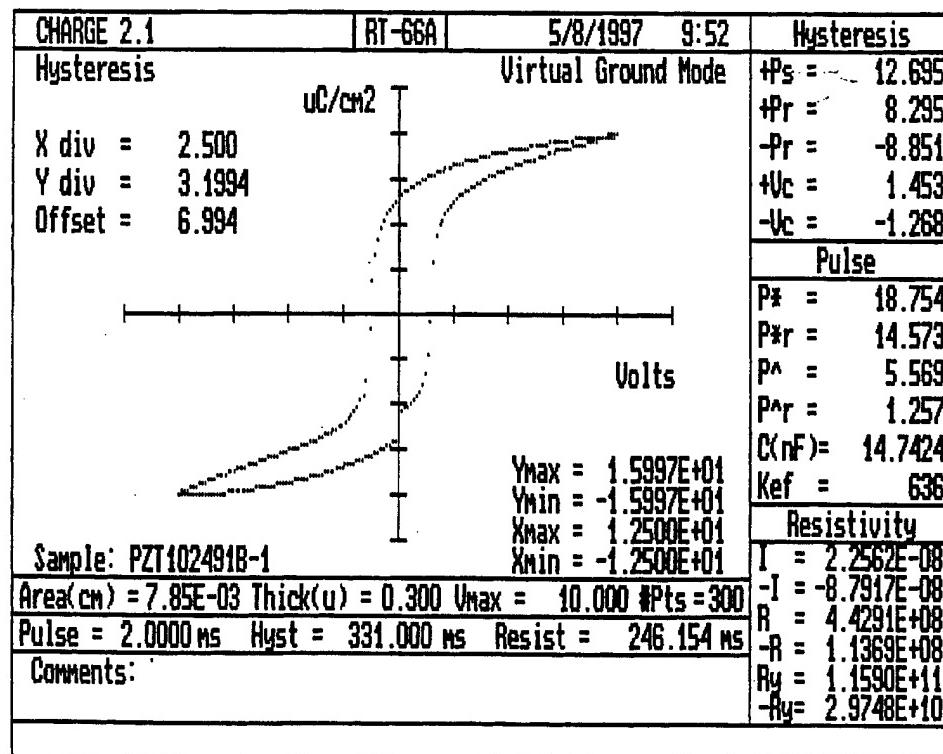
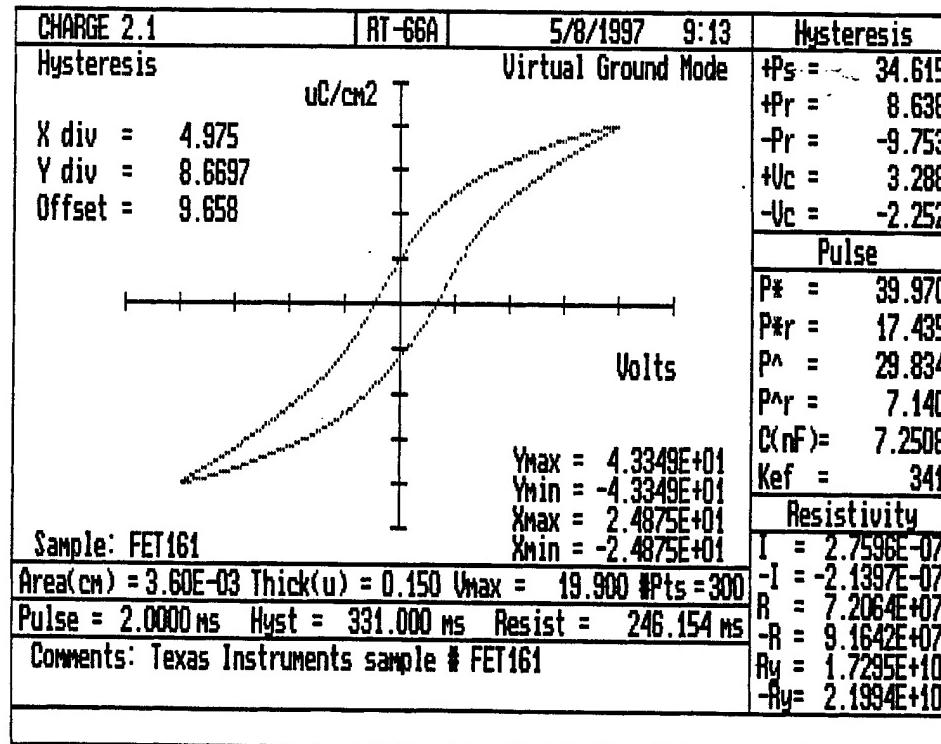


Figure 6. Hysteresis loop of typical RTIS sample (sample FET 161).



The very low resistivities of samples 164 and 280 most certainly lie in the large excess of lead in these samples. Both of these samples had concentrations of lead 20 percent above stoichiometry. All the rest had 10-percent excess lead above stoichiometry. Clearly, 20-percent excess lead has a deleterious effect on film performance, where 10-percent excess yields films with good properties. Films 164 and 280 also yielded hysteresis loops that saturated at more typical voltages (20 to 24 V peak-to-peak), rather than the 40 V peak-to-peak observed in the other samples. Some of the pads on both these samples leaked current so badly that they were visibly damaged by the current passing through them.

RTIS has also experimented with more complex substituted PLZT systems. Substitutions of Ca or Ba in the A-site in the perovskite structure, in place of Pb, result in marked improvements in material performance. Likewise, substitution of Sn in the B-site, in place of Ti, also results in further improved performance. A typical hysteresis loop of one of these films is shown in figure 7. Substantial decreases in the dissipation factor and the dielectric constant have been observed when Ba or Ca is substituted in the A-site (table 3). Increasing Ba from 10 to 20 mol % results in a decrease in ϵ_r from 140 to 110, and $\tan \delta$ decreases from 0.016 to 0.010. Substitution of Ca in the A-site lowered ϵ_r from 89 to 80 and $\tan \delta$ actually increased somewhat from 0.007 to 0.026. Double substitution of Ca in site A and Sn in site B allows for even greater improvement in the properties. A 10%Ca/10%Sn substitution maintained a low ϵ_r of 79 and a $\tan \delta$ of about 0.012. However, there was a marked improvement in the pyroelectric coefficient p up to about 24 nC/cm²-K. This corresponds to a noise equivalent temperature difference (NETD) of about 15 mK for a 48.5-μm pixel and 28.6 mK for a 25-μm pixel. A 20%Ca/10%Sn substitution also maintains ϵ_r and $\tan \delta$ at 103 and 0.009, respectively, corresponding to an NETD of 13.8 mK for a 48.5-μm pixel and 26.5 mK for a 25-μm pixel.

We also investigated the effect of multiple cycles on the shape of the hysteresis loop and the dielectric measurements obtained. Measurements taken at 9 V yielded the smaller loop in figure 8. Increasing the voltage to 12 V yielded the larger loops in figure 8. This family of loops was created by three successive cycles of the instrument, and shows that the film changes characteristics with each successive cycle. The same measurement done at 9 V showed no such differences. Therefore, it would appear that the film is degraded when subjected to higher voltages during cycling.

Figure 7. RTIS sample PBT-10 showing asymmetric hysteresis loop.

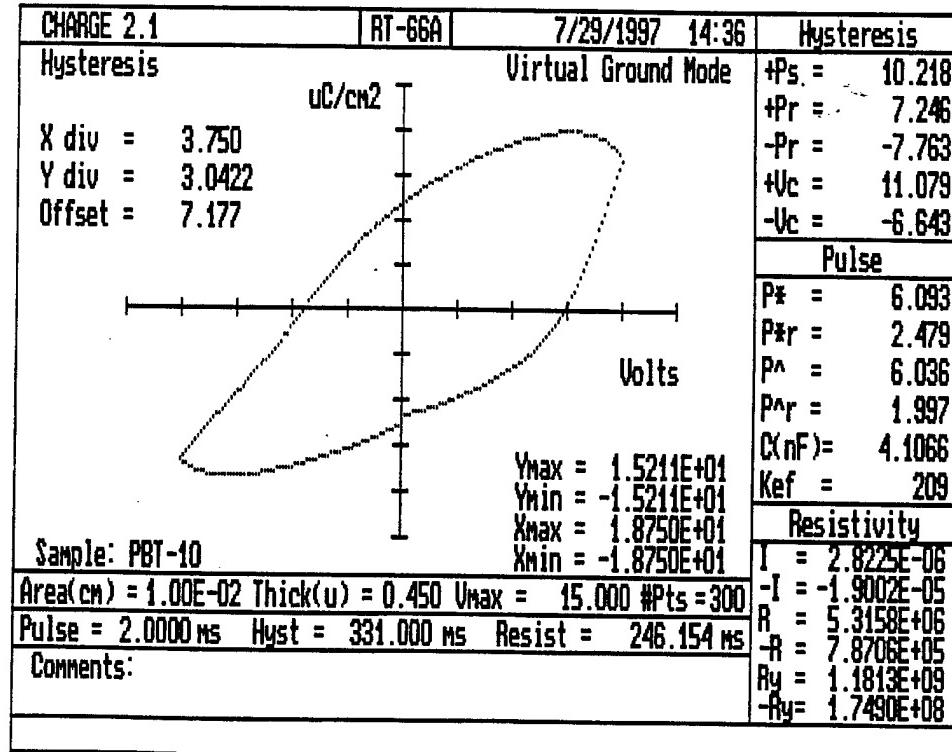
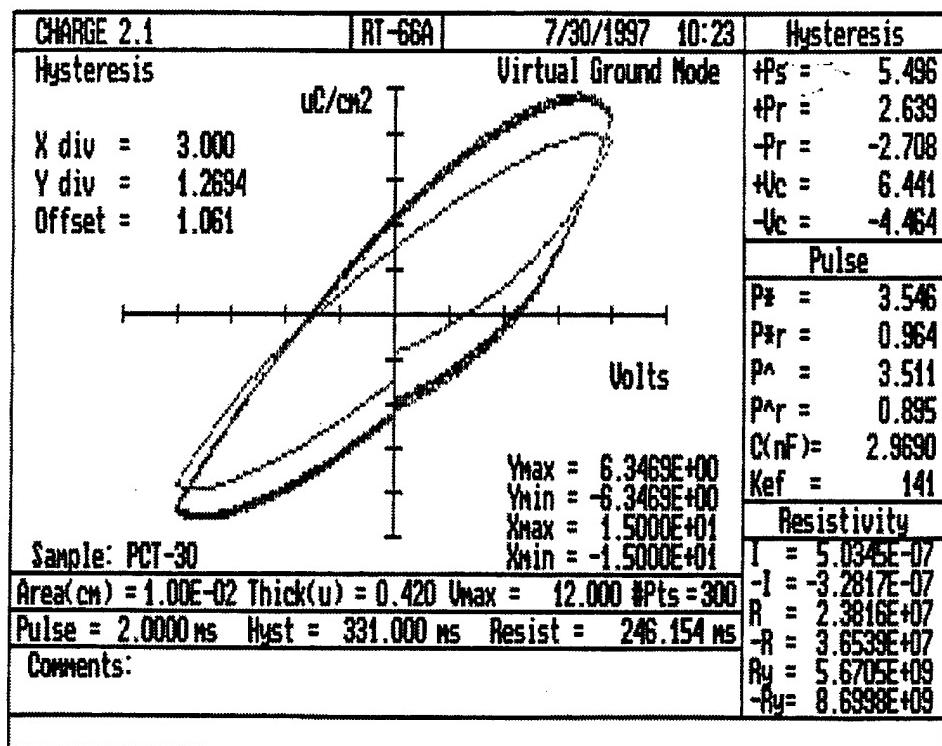


Table 3. Electrical properties of substituted lead titanates.

Sample	Thickness (μm)	ϵ_r	$\tan \delta$	p (nC/cm ² -K)	Figure of merit ($\times 10^5$ Pa ^{-1/2})	Projected NETD (mK)	
						48.5 μm	25 μm
PBT-10	0.25	140	0.016	19.5	1.62	21.7	41.5
PBT-20	0.38	110	0.01	14.5	1.72	22.3	46.7
PCT-10	0.43	89	0.007	14.3	2.26	23.4	41.9
PCT-30	0.46	80	0.026	16.6	1.43	26.9	50.8
PCSnT-10/10	0.37	79	0.012	23.5	3.00	15.0	28.6
PCSnT-20/10	0.31	103	0.009	26.7	3.45	13.8	26.5

Figure 8. Hysteresis loop of RTIS sample PCT-30 showing effect of multiple cycles.



5. Conclusions

At this time, we do not know what the complete ramifications of the anomalies are for device performance. However, in the sensor array, the thin film will be poled to maximize the pyroelectric current generated, and any asymmetry or imprinting in the hysteresis loop should not adversely affect overall array performance. RTIS maintains that the consistently high pyroelectric coefficients measured readily offset the unusual behavior observed in the hysteresis data. Once poled, the film essentially will be maintained at that particular point in the hysteresis loop indefinitely.

With regard to the dielectric constant ($\epsilon < 500$), the first-year goals have been met or exceeded. However, in most cases, the loss tangent is higher than the goal ($\tan \delta > 0.02$), although some of the samples exceeded the first-year goal. It is best to keep in mind that the samples tested for this report may not be wholly representative of the entire sample set. It also appears that the electrode system that RTIS used and its manner of deposition is crucial to device performance as well, but the largest changes and anomalies occurred when the lead was increased from 10 percent above stoichiometry to 20 percent.

RTIS is steadily approaching the 10-mK goal, having achieved 13.8 mK for 48.5- μ m pixels, and 26.5 mK for 50- μ m pixels. With continuing improvements in materials and processing, we are reasonably confident that RTIS will reach the 10-mK performance goal at the end of the three-year contract period.

In the near future we will test these samples to measure the pyroelectric coefficient of the samples supplied by RTIS. This test will enable ARL to independently calculate figures of merit and the NETD of samples produced under contract, as well as to evaluate samples of new materials grown in-house.

Distribution

Admnstr
Defns Techl Info Ctr
Attn DTIC-OCP
8725 John J Kingman Rd Ste 0944
FT Belvoir VA 22060-6218

Ofc of the Dir Rsrch and Engrg
Attn R Menz
Pentagon Rm 3E1089
Washington DC 20301-3080

Ofc of the Secy of Defns
Attn ODDRE (R&AT) G Singley
Attn ODDRE (R&AT) S Gontarek
The Pentagon
Washington DC 20301-3080

OSD
Attn OUSD(A&T)/ODDDR&E(R) R Tru
Washington DC 20301-7100

Army Rsrch Physics Div
Attn AMXRO-PH D Skatrud
Research Triangle Park NC 27709

ARPA
Attn R Balcerak
3701 N Fairfax Dr
Arlington VA 22203-1714

CECOM
Attn PM GPS COL S Young
FT Monmouth NJ 07703

CECOM RDEC Elect System Div Dir
Attn J Niemela
FT Monmouth NJ 07703

CECOM
Sp & Terrestrial Commctn Div
Attn AMSEL-RD-ST-MC-M H Soicher
FT Monmouth NJ 07703-5203

Dir of Assessment and Eval
Attn SARD-ZD H K Fallin Jr
103 Army Pentagon Rm 2E673
Washington DC 20301-0163

Hdqtrs Dept of the Army
Attn DAMO-FDT D Schmidt
400 Army Pentagon Rm 3C514
Washington DC 20301-0460

MICOM RDEC
Attn AMSMI-RD W C McCorkle
Redstone Arsenal AL 35898-5240

US Army Avn Rsrch, Dev, & Engrg Ctr
Attn T L House
4300 Goodfellow Blvd
St Louis MO 63120-1798

US Army CECOM Rsrch, Dev, & Engrg Ctr
Attn R F Giordano
FT Monmouth NJ 07703-5201

US Army Edgewood Rsrch, Dev, & Engrg Ctr
Attn SCBRD-TD J Vervier
Aberdeen Proving Ground MD 21010-5423

US Army Info Sys Engrg Cmnd
Attn ASQB-OTD F Jenia
FT Huachuca AZ 85613-5300

US Army Materiel Sys Analysis Agency
Attn AMXSY-D J McCarthy
Aberdeen Proving Ground MD 21005-5071

US Army Matl Cmnd
Dpty CG for RDE Hdqtrs
Attn AMCRD BG Beauchamp
5001 Eisenhower Ave
Alexandria VA 22333-0001

US Army Matl Cmnd
Prin Dpty for Acquisition Hdqrts
Attn AMCDCG-A D Adams
5001 Eisenhower Ave
Alexandria VA 22333-0001

US Army Matl Cmnd
Prin Dpty for Techlgy Hdqrts
Attn AMCDCG-T M Fisette
5001 Eisenhower Ave
Alexandria VA 22333-0001

Distribution

US Army Natick Rsrch, Dev, & Engrg Ctr Acting Techl Dir Attn SSCNC-T P Brandler Natick MA 01760-5002	GPS Joint Prog Ofc Dir Attn COL J Clay 2435 Vela Way Ste 1613 Los Angeles AFB CA 90245-5500
US Army Rsrch Ofc Attn G Iafrate 4300 S Miami Blvd Research Triangle Park NC 27709	DARPA Attn B Kaspar Attn L Stotts 3701 N Fairfax Dr Arlington VA 22203-1714
US Army Simulation, Train, & Instrmntn Cmnd Attn J Stahl 12350 Research Parkway Orlando FL 32826-3726	ARL Electromag Group Attn Campus Mail Code F0250 A Tucker University of Texas Austin TX 78712
US Army Tank-Automtv & Armaments Cmnd Attn AMSTA-AR-TD C Spinelli Bldg 1 Picatinny Arsenal NJ 07806-5000	Dir for MANPRINT Ofc of the Deputy Chief of Staff for Prsnnl Attn J Hiller The Pentagon Rm 2C733 Washington DC 20301-0300
US Army Tank-Automtv Cmnd Rsrch, Dev, & Engrg Ctr Attn AMSTA-TA J Chapin Warren MI 48397-5000	NVESD Attn AMSEL-RD-NV-ST-IRT J E Miller Attn AMSEL-RD-NV-ST-IRT S Horn 10221 Burbeck Rd FT Belvoir VA 22060-5806
US Army Test & Eval Cmnd Attn R G Pollard III Aberdeen Proving Ground MD 21005-5055	Raytheon TI Systems Attn C Hanson 13532 N Central Expy MS 37 Dallas TX 75265
US Army Train & Doctrine Cmnd Battle Lab Integration & Techl Dircrt Attn ATCD-B J A Klevecz FT Monroe VA 23651-5850	US Army Rsrch Lab Attn AMSRL-CI-LL Techl Lib (3 copies) Attn AMSRL-CS-AL-TA Mail & Records Mgmt Attn AMSRL-CS-AL-TP Techl Pub (3 copies) Attn AMSRL-SE-EP R C Hoffman (2 copies) Attn AMSRL-SE-EP W Tipton (2 copies) Adelphi MD 20783-1197
US Military Academy Dept of Mathematical Sci Attn MAJ D Engen West Point NY 10996	
USAASA Attn MOAS-AI W Parron 9325 Gunston Rd Ste N319 FT Belvoir VA 22060-5582	
Nav Surface Warfare Ctr Attn Code B07 J Pennella 17320 Dahlgren Rd Bldg 1470 Rm 1101 Dahlgren VA 22448-5100	

REPORT DOCUMENTATION PAGE			<i>Form Approved OMB No. 0704-0188</i>
<p>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</p>			
1. AGENCY USE ONLY <i>(Leave blank)</i>	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	February 1998	Progress, from July 1996 to July 1997	
4. TITLE AND SUBTITLE		5. FUNDING NUMBERS	
Analysis of Ferroelectric Thin Films Grown by MOD Process		PE: 62705A	
6. AUTHOR(S)		DAAL01-96-C-0076	
Robert Hoffman and Wesley Tipton			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)		8. PERFORMING ORGANIZATION REPORT NUMBER	
U.S. Army Research Laboratory Attn: AMSRL-SE-EP (e-mail: bhoffman@arl.mil) 2800 Powder Mill Road Adelphi, MD 20783-1197		ARL-MR-375	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
Defense Advanced Research Projects Agency 3701 N. Fairfax Drive Arlington, VA 22203			
11. SUPPLEMENTARY NOTES			
AMS code: 622705.H94 ARL PR: 8NE6BB			
12a. DISTRIBUTION/AVAILABILITY STATEMENT		12b. DISTRIBUTION CODE	
Approved for public release; distribution unlimited.			
13. ABSTRACT <i>(Maximum 200 words)</i>			
<p>The Army Research Laboratory (ARL) has performed ferroelectric characterization testing of thin film ferroelectric samples provided by Raytheon TI Systems (RTIS) for the DARPA (Defense Advanced Research Projects Agency) uncooled detector materials program. The samples measured at ARL, produced by the metal-organic decomposition (MOD) method, have hysteresis loop characteristics, remanant polarization, and dielectric constant and resistivity values commensurate with measurements made at RTIS. RTIS projections show that Ca- and Sn-doped samples should achieve a projected noise equivalent temperature difference (NETD) of 13.8 mK with 48.5-μm pixels and 26.5 mK with 50-μm pixels, respectively.</p>			
14. SUBJECT TERMS		15. NUMBER OF PAGES 19	
Uncooled, infrared		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL